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Research into the Variables Affecting Purge and Trap Collection for a Portable Field Trihalomethane Testing Unit

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Research into the Variables Affecting Purge and Trap Collection for a Portable Field Trihalomethane Testing Unit

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Abstract

Trihalomethanes are a group of chemicals formed when chlorine reacts with naturally occurring organic matter and bromide. The Environmental Protection Agency has recently published the Stage 1 Disinfectants/Disinfectation Byproducts Rule to regulate total trihalomethanes at a maximum allowable annual average level of 80 parts per million. Current methods for trihalomethane testing are costly and slow. They have been primarily used in the imposition of fines. As a result, Sandia National Laboratories has developed a cost-effective portable testing unit to detect volatile organic compounds via purge and trap, gas chromatography, and surface acoustic wave detection. The research discussed in this report investigates some of the variables unique to a portable testing device. We have determined three things. First, environmental air can be used as a substitute for helium as a purging gas. Second, the majority of THM removal occurs during the first five minutes of purging. Third, a metal reservoir can be used as a substitute for glass.

Acknowledgments

Looking back at the last year and a half, I am amazed at the number of people who have contributed in a variety of ways to the success of this project. First, and most importantly, I need thank the members of my committee: Dr. Mary Walker (University of New Mexico), Dr. Graham Timmins (University of New Mexico), and Dr. Curtis Mowry (Sandia National Laboratories). I additionally owe Dr. Walker a warm thank you for serving as my advisor over the last two years and navigating me through the M.S. Pharmaceutical Sciences program at UNM.

I am extremely grateful to Curt for including me in the development of this LDRD. Although I learned a tremendous amount about trihalomethane compounds, the greatest lessons have been in the concepts of basic research. I have learned how to develop a hypothesis, conduct relevant experiments, and analyze data to draw conclusions. These lessons have only been possible because of my talented co-workers. I specifically thank Ted Borek and Steve Meserole for their guidance. I further extend thanks to Ted for the use of his instruments, laboratory space, and for bringing me to Sandia almost three years ago.

In addition to the funding provided by LDRD 52595, this project also relied upon the Waste Education and Research Consortium (WERC). WERC helped pay for part of the data analysis and the writing of this project.

I finally need to thank my family and friends for their support over the last two years.

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Acronyms and Abbreviations

American Water Works Association (AWWA)
automated thermal desoption (ATD)
Department of Energy (DOE)
deoxyribonucleic acid (DNA)
disinfection by-products (DBP)
Environmental Protection Agency (EPA)
gas chromatography (GC)
Hewlett-Packard (HP)
mass spectrometry (MS)
methyl tert-butyl ether (MTBE)
milliliter (mL)
nanogram (ng)
natural organic matter (NOM)
parts per billion (ppb)
parts per million (ppm)
purge and trap (P&T)
Sandia National Laboratories (SNL)
surface acoustic wave (SAW)
trihalomethane (THM)
ultraviolet (UV)
Water Analysis Surety Prototype (WASP)

Introduction

The implementation of chlorination systems has virtually eliminated water borne disease in the United States. However, trihalomethanes (THM's) formed when hypochlorous acid reacts with bromide and natural organic matter might pose different health risks as many have proven to be carcinogenic. These concerns have led the Environmental Protection Agency (EPA) to instigate new regulations that lower the maximum annual allowable total THM level and require testing to occur more frequently. Current methods for THM testing are costly and slow; they have been primarily used in the imposition of fines. As a result, Sandia National Laboratories (SNL) has developed a cost-effective portable testing unit to detect volatile organic compounds via purge and trap, gas chromatography, and surface acoustic wave detection. The research discussed in this report investigates some of the variables unique to a portable testing device. These include purge time, purging gas, and reservoir composition.

Background and Significance

One of the greatest advances in public health has been the discovery of waterborne disease and the widespread implementation of water disinfection systems[1]. This practice first began in 1850 when John Snow attempted to use chlorine to disinfect the Broad Street Pump water supply in London after an outbreak of cholera. Sim Woodhead then followed by using a "bleach solution" to sanitize water distribution mains in Maidstone, Kent following a typhoid outbreak. The success of these two instances in preventing the spread of disease encouraged Great Britain to construct the first continuous chlorination water treatment systems in the early twentieth century. In North America, the concept first began in Jersey City, N.J during 1908. Adoption by other cities and towns across the United States soon followed and by the end of the 1920s had resulted in a 85% drop in the number of typhoid deaths.[2] Over the last century, drinking water disinfection has played an essential role in the virtual elimination of waterborne disease in the United States. This is in sharp contrast to developing countries where unimproved water still annually effects the health of about 1.2 billion people[3] and contributes of the death of 15 million children under the age of five.[4] Table 1 lists some common microorganisms found in wastewater and the associated diseases.

Over the years, a number of treatment processes have been developed. These processes include chlorination, ultraviolet (UV) radiation, and ozonation.

- *Chlorination*: Chlorine is added to drinking water as elemental chlorine or sodium hypochlorite. These forms of "free chlorine" react with water to produce the strong oxidants hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). These compounds then oxidize the pathogen's cellular membrane causing cell lysis. The hypochlorite ion is able to further disassociate into oxygen (O) and chlorine (Cl^-). Chlorine can then replace hydrogen atoms located in cellular proteins and enzymes via substitution reactions. This

substitutions cause changes protein conformation and intra-cellular balances to be disrupted.[5]

- *UV radiation*: Water is typically exposed to light at 254 nm. This wavelength corresponds to one of two peaks on the germicidal effectiveness cure or the wavelength where UV light is absorbed by DNA. When UV light is absorbed by DNA it causes adjacent thymine molecules to dimerize. These defects accumulate in a microorganism's DNA causing its replication to be inhibited. The organism is rendered harmless even through it may be not be killed outright.[6]
- *Ozone disinfection*: Most wastewater treatment facilities generate ozone by imposing a high voltage alternating current across a gap containing oxygen gas. This causes oxygen (O_2) molecules to dissociate into oxygen atoms, collide with a second oxygen molecule, and form ozone (O_3) gas. Ozone is strong oxidant that will inactivate or destroy microorganisms through destruction of their cellular wall and/or damage to their nucleic acids.[7]

Table 1: Infectious Agents Potentially Present in Untreated Wastewater.

Organism	Disease Caused
Bacteria	
Escherichia coli	Gastroenteritis
Leptospire	Leptospirosis
Salmonella typhi	Typhoid Fever
Salmonella	Salmonellosis
Shigella	Shigellosis
Vibrio cholerae	Cholera
Protozoa	
Balantidium coli	Balantidiasis
Cryptosporidium parvum	Cryptosporidiosis
Entamoeba histolytica	Amoebic dysentery
Giardia lamblia	Giadiasis
Helminths	
Ascaris lumbricoides	Ascariasis
T. solium	Taeniasis
Trichuris trichiura	Trichuriasis
Viruses	
Enteroviruses	Gastroenteritis, heart anomalies, meningitis
Hepatitis A virus	Hepatitis
Norwalk agent	Gastroenteritis
Rotavirus	Gastroenteritis

Despite the variety of methods available, chlorination remains the most widely accepted method for several reasons. First, chlorine is effective against a broad spectrum of problems. In addition to killing pathogens, such as bacteria, viruses, and protozoa, chlorination can also control odor, prevent algae growth, and improve taste. Second, chlorine provides residual protection. Hypochlorous acid and hypochlorite ion are relatively stable. This allows for protection against microbial growth after the treated

water enters distribution systems[8]. Third, chlorine has well understood operational requirements and has been shown to be reliable in water treatment plants of all sizes.[9,10]

Although chlorination has done wonders to reduce disease caused by waterborne microbes, it is not without controversy. Chlorination produces disinfection by-products (DBPs) that are of potential health concern. These DBPs are formed when hypochlorous acid (HOCl) generated during water treatment reacts with bromide (Br^-) and natural organic matter (NOM) in surface water. NOM arises from decaying vegetation and algae while bromide is derived from natural (e.g., mineral deposits and salt water intrusions) or human-induced (e.g, agricultural use of methyl bromide and use of salts to prevent ice formation on roads) sources.[11, 12] When these three elements interact, hypochlorous acid rapidly oxidizes bromide to hypobromous acid which in turn reacts with the precursor materials to produce mixed chloro-bromo substitution products or halogenated DBPs.[13, 14]

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

$$HOCl + Br^- + NOM \rightarrow \text{Halogenated DBPs}$$

The two main categories of disinfection by-products are trihalomethanes (THMs) and haloacetic acids (HAAs). The four THMs are chloroform ($CHCl_3$), bromo-dichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). Their structures are visible in Figure 1. The five HAAs regulated by the EPA are monochloroacetic acid ($C_2H_3ClO_2$), dichloroacetic acid ($C_2H_2Cl_2O_2$), trichloroacetic acid ($C_2HCl_3O_2$), monobromoacetic acid ($C_2H_3BrO_2$), and dibromoacetic acid ($C_2H_2Br_2O_2$).

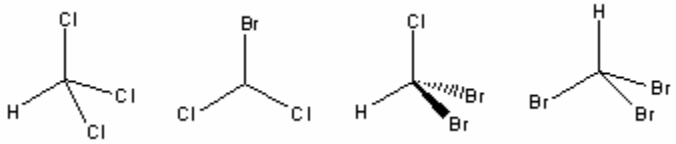

Figure 1: THM Structures.
Left to right: chloroform, dichlorobromomethane, dibromochloromethane, bromoform

Over the last decade, epidemiological and experimental studies have reported a relationship between THM and HAA exposure to a variety of health concerns. These concerns include reproductive endpoints, developmental defects, and cancer. The conclusions of a few of these studies are summarized below.

- Chloroform exposure caused liver and renal tumors in laboratory mice and rats.[15]
- Drinking water DBPs have been associated with an increased risk for congenital defects. This is particularly true of cardiac defects.[16]
- THM exposure has been linked with spontaneous abortion.[17]
- A positive association has been viewed between consumption of chlorinated drinking water and cancer of the rectum, lung, bladder, and kidney.[18]

- Exposure to DBPs in drinking water has been associated with an increased risk of bladder cancer.[19]

Adding to the controversy are studies indicating that ingestion is not the only significant exposure route to DBPs. Exposure can also occur through inhalation and dermal absorption.[10] This accumulation of evidence coupled with the large number of people exposed has caused the EPA to propose additional DBP control measures. Under the Stage 1 "Disinfectant/Disinfection By-Product Rule" the annual maximum allowable THM exposure level is lowered from 100 ppb to 80 ppb, an annual maximum allowable HAA exposure level of 60 ppb is instigated, and testing of public water systems is required to occur more frequently.[10,8] The compliance deadline was January 2004. Unfortunately, current methods available for THM and HAA collection and analysis are costly and slow. They are used primarily in the imposition of fines and do not lend themselves to the EPA's stricter testing requirements. As a result, the annual cost of this change is expected to be between $54.3 to 63.9 million with public water systems bearing approximately ninety-eight percent of the total cost.[20]

Sandia National Laboratories has developed a portable testing unit, nicknamed Water Analysis Surety Prototype (WASP) to detect THMs via gas-phase sampling. The unit is visible as

Figure **2** and Figure 3. This unit collects THMs on a miniature pre-concentrator, separates them with a gas chromatography column, and identifies them using surface acoustic wave (SAW) detection[a]. The THMs are removed from aqueous solution using purge and trap. In purge and trap, an inert gas is bubbled through a water sample causing organics to move from the aqueous to vapor phase.[21] The THMs are then collected on an absorbent trap. The trap is then placed in an automated thermal desorption (ATD) unit where it is heated to release THM compounds. The procedure is a variation of that outlined in EPA Method 524.2 and the American Water Works Association (AWWA) Method 6200.

> "This is a general purpose method for the identification and simultaneous measurement of purgeable volatile compounds in surface water, ground water, and drinking water in any stage of treatment." EPA Method 524.2

Table 2 and Figure 4 outline some of the similarities and differences between EPA Method 524.2 and Sandia National Laboratory's field system. It is from these differences that the specific aims for this project are generated. Each aim manipulates one variable described later in Table 2.

[a] SAW detectors are quartz crystals having patterned electrodes that allow a high frequency (25-500 MHz) wave to be maintained on their surface. The crystal frequency is primarily based on the spacing of the electrodes. Since this pattern remains fixed, the frequency remains constant until a material is absorbed by the surface. This enables the SAW to sense mass and mechanical properties.

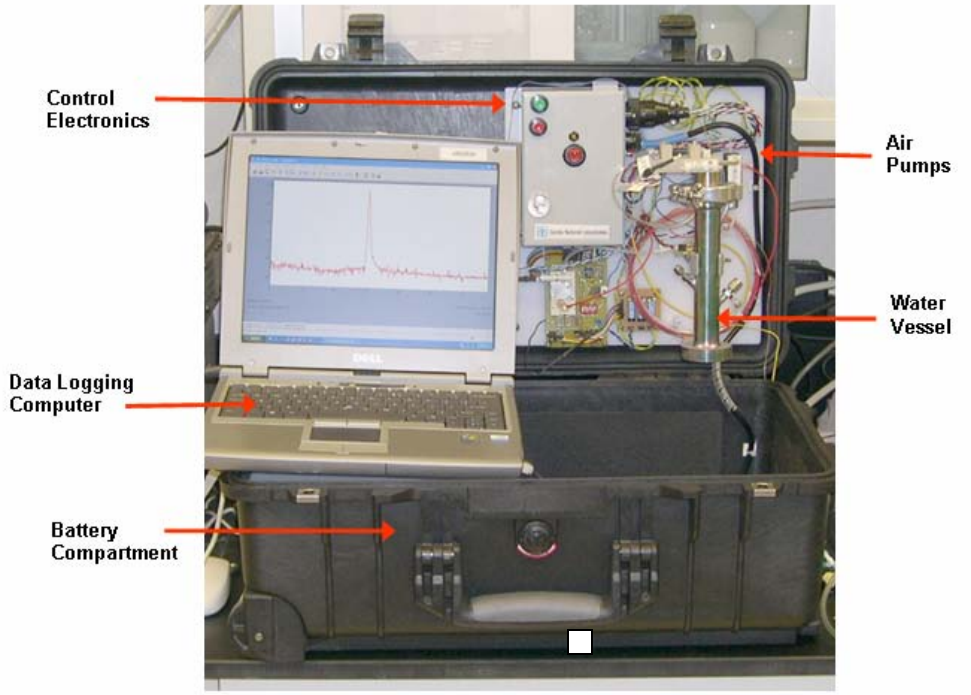

Figure 2: Photo of Final Field THM Detection System.

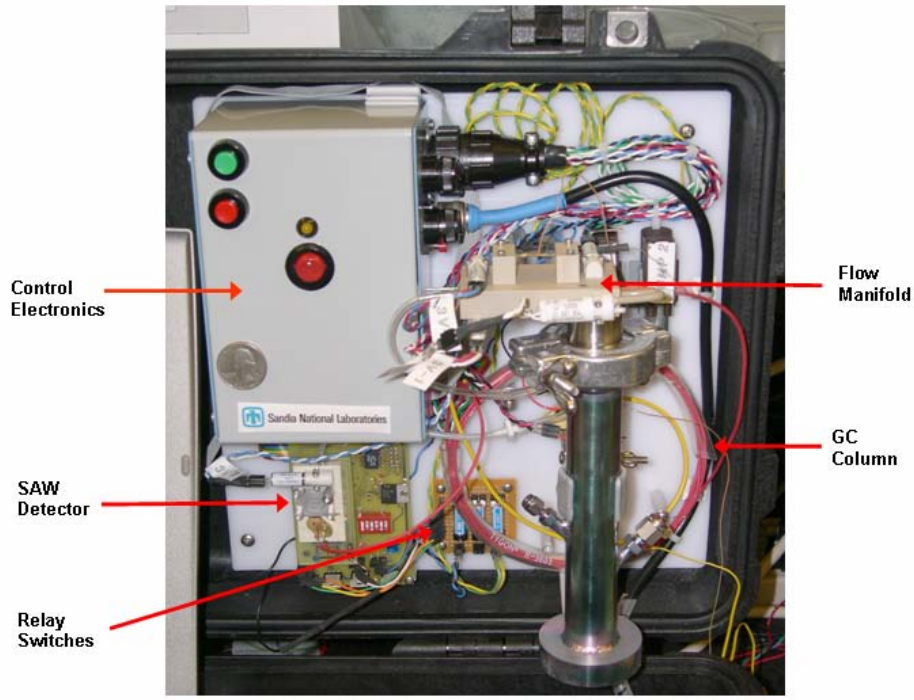

Figure 3: Close-Up Photo of Fluidics, Electronics, and Water Vessel.

Table 2: Comparison between EPA Method 524.2 and Field System Parameters.

Characteristic	EPA	Field System
Water Sample Size	5 or 25 mL	50 mL
Bubbling Gas	helium	air
Flow	40 cc	40 cc
Purge Time	11 min	1 to 3 min preferably
Air Temperature	ambient	environmental conditions (0 to 100 ºC)
Absorbent Trap	activated charcoal, silica gel, methyl silicon packing, 2,6-dipheylene polymer	hayesep D[a]
Sample Vessel	glass	metal

[a]Hayesep D is a high purity divinylbenzene polymer typically used in the separation of light gases. It is the preconcentor in the field system. For the experiments in this paper, commercially purchased Tenax TA® desorption tubes were utilized.

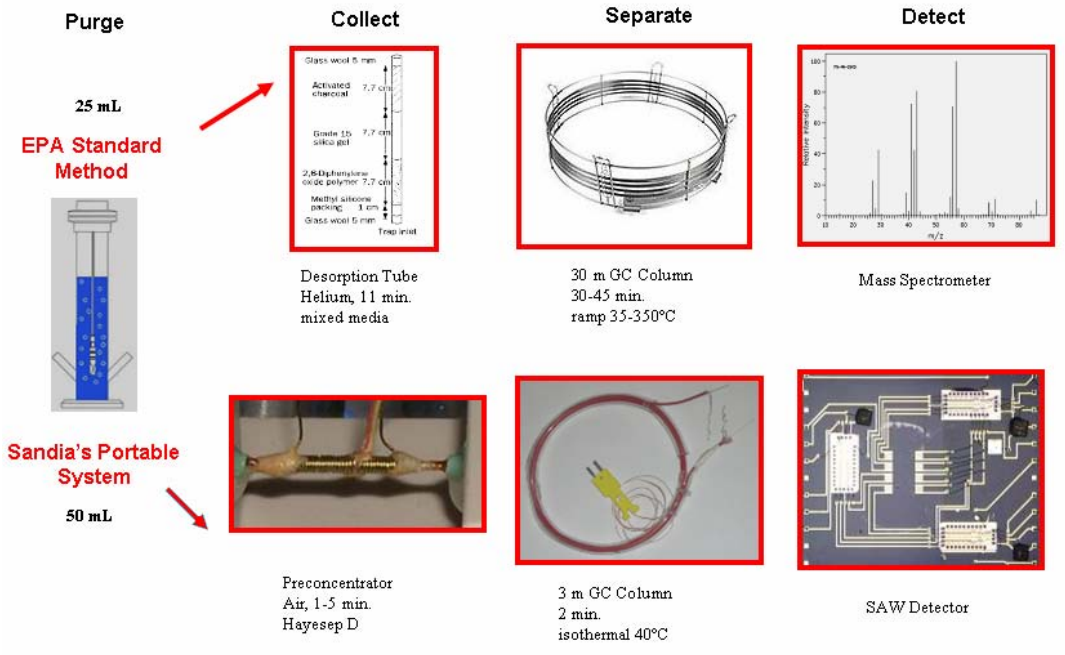

Figure 4: THM Detection Methods: Laboratory vs Field.[22]
Adapted with permission from Curtis D. Mowry

HAAs were not the focus of WASP. They are less volatile and typically have tailing unsymmetrical chromatograph peaks.[22] This makes them more difficult to analyze by gas chromatography. In the laboratory, the standard method is to derivatize them to a less polar compound. This process is not possible for field analysis. Although method development occurred regarding the application of WASP to HAAs, it is not addressed in this report.

B. Specific Aims and Hypotheses

1. Compare the THM purging efficiency of compressed air and helium. Current EPA Method 524.2 uses helium as the purging gas. However, the use of helium is not convenient in a field system. Space for a helium cylinder and its respective hardware are not readily available in a portable system. This aim will test environmental air to see if it is a suitable substitute.

   It is hypothesized that compressed air and helium will not have similar purging efficiencies. Helium is a monatomic gas while compressed air is primarily composed of the diatomic molecules oxygen and nitrogen. These molecules have a dipole moment that provides a greater opportunity to interact with molecules in the water samples. However, THMs are extremely volatile. The literature reports mean recovery values of one hundred percent for all four THMs.[21, 23] Even if compressed air decreases efficacy, the recovery should still be above the detection limit of the SAW.

2. Evaluate how purge time affects the amount of THM compounds collected. Current EPA Method 524.2 calls for a purging time of eleven minutes. A purge of this length requires significant battery power potentially consuming limited energy resources. A shorter purge time would also help to maximize the number of samples processed. This aim attempts to find the point where enough THMs have been removed for reliable SAW detection while minimizing energy expenditure.

   We hypothesize purging time will effect the amount of THMs collected. Since THMs are extremely volatile the majority will be collected within the first few minutes. Collection of THM is hypothesized to follow the Law of Diminishing Returns that describes how continued effort toward a particular goal will decline in effectiveness after a certain level of result has been achieved. This aim attempts describe the length where ratio of THM collection to time is the greatest. This is likely to be under 5 minutes.

3. Determine if the reservoir composition is important. Current EPA Method 524.2 call for purging apparatus to be made of glass. Glass is not practical in a field system due to breakability. If a vessel breaks and no replacement is available, sample analysis is delayed causing a waste of time and money. In addition, broken glass could damage the field system and contaminate the environment. This aim evaluates the use of stainless steel as a viable alternate.

   We hypothesize that metal should be an acceptable substitute. Unlike Teflon or a variety of other materials, EPA Method 524.2 does not prohibit the use of stainless steel tubing. In addition, stainless steel is used in a variety of commercial systems. There is not reason to believe interactions would uniquely occur in the water vessel.

C. Methods

3.1 Reagents

THMs were purchased as a mixture from Ultra Scientific Analytical Solutions (Kingstown, RI) at a 100 µg/mL concentration in methanol. Working standard solutions were prepared by diluting the methanolic standards with high quality water obtained using a Milli-Q water purification system. Both purchased and working standards were refrigerated or kept on ice when not in use. Anhydrous chloroform was purchased from Sigma-Aldrich (Milwaukee, WI).

3.2 Purge-and-Trap Design and Instrumentation

The two purge-and-trap designs used to test the specific aims are visible as Figure 5 and Figure 6. In the first system, a gas cylinder and appropriate regulator are connected to 1/8 inch sulfinert stainless steel tubing (Restek, Bellefonte, PA). The tubing then connects to a needle valve (Albuquerque Valve and Fitting, Albuquerque, NM) that reduces the gas flow to 60-65 cc and a three-way valve (Albuquerque Valve and Fitting, Albuquerque, NM). The three-way valve is used to by-pass the bubbling system so samples can be changed without stopping gas flow. The tubing then attaches to a gas bubbler that directs the gas flow through a glass frit and into 25 mL of sample water. Compressed helium and air cylinders were purchased from Matheson TriGas (Irving, TX). The sample water is kept at a constant temperature using a Neslab Endocal RST-110 constant temperature bath (Thermo Electron Corp, Waltham, MA). Commercially packed Tenax TA®[b] desorption tubes were purchased from Altech (Deerfield, IL) and used for THM collection. Although EPA Method 524.2 suggests tubes self-packed with activated charcoal, silica gel, methyl silicon packing, and 2,6-diphenylene polymer, Tenax TA® tubes have been experimentally demonstrated as equivalent for the purge and trap analysis of THMs.[21, 24-32] A flow measurement is recorded from the end of the desorption tube by an Altech Digital Flow Check (Deerfield, IL).

In the second system, a miniature pump powered by an Agilent Dual Output DC Power Supply (Palo Alto, CA) is used to pull laboratory air through the Tenax TA® desorption tube and sample. The stainless steel tubing, glass frit, and flow meter described above were used. The second purge and trap system was an attempt to more closely mirror the field unit. Instead of using a compressed gas cylinder to push air through the bubbler, this system utilizes a pump to pull air through. The second system also lessened the flow consistency problems discussed in the Aim 1 results section.

After THM collection, the Tenax TA® tube was removed and analyzed with a Perkin-Elmer 400 automated thermal desorption unit (ATD), Hewlett-Packard (HP) 5891 gas chromatograph, and HP-5972 series mass spectrometer. The HP GC/MS is supported by ChemStation system software. The analytical conditions of the gas chromatograph-

[b] Tenax TA® is a porous polymer resin based on 2,6-dipenylene oxide. It has been specifically designed for the trapping of volatile and semi-volatile compounds from air which have been purged from liquid or solid sample matrices. Due to its low affinity for water, Tenax TA® is especially useful for the purging and trapping volatiles from high moisture content samples. Its temperature limit is 350˚C.

mass spectrometer are presented in Table 3. Selective ion monitoring was used to increase sensitivity.[33]

Table 3: Experimental Conditions of the PT-GC-MS System.

PT Conditions	Sample volume	25 mL
	Gas flow	40 mL min^{-1}
	Temperature	Ambient
	Trap material	Tenax TA
Desorption Conditions	Desorb cylce	10 min at 225ºC
	Transfer Line	220ºC
GC Conditions	Injection port	240ºC
	Capillary column	Alltech DD-5; length, 60 m; i.d., 0.32 mm
	Carrier gas	Helium with a flow rate of 1.6 mL/min
	Oven program	Initial Temp, 35ºC for 7 min. Increased by 4ºC/min to 140ºC. Increased by 20ºC/min to 250ºC. Held for 10 min.
MS Conditions	SIM	
	Chloroform	47, 83, 85 m/z
	Dichlorobromomethane	47, 83, 85, 129 m/z
	Dibromochloromethane	127, 129, 131 m/z
	Bromoform	92, 173, 253 m/z

Tenax TA® tubes were cleaned after each use with a Dynatherm Analytic Instruments Inc Model 60 six-tube conditioner (CDS Analytical Inc, Oxford, PA). They were cleaned at 240ºC for 50 minutes while purged with helium at flow of 60 to 70 mL/min. One tube per condition session was run on the GC/MS to ensure to no residual THM remained. A chromatograph of a clean Tenax TA® tube is visible as Figure 7. Water blanks were also collected between samples to ensure no residual THM compounds remained in the system.

3.3 Calibration Curve

A calibration curve was generated using 100, 500, and 1000 ng of each THM. A VWR Scientific Inc Microdispensor (Westchester, PA) was used to dispense 1 ± 0.01 5 ± 0.05, or 10 ± .1 µL onto a Tenax TA® desorption tube. The Tenax TA® tube was then run on the ATD/GC/MS under the same conditions as samples. Peak area for each standard was then plotted against total nanograms and a linear regression line was applied. The calibration curve for each THM is visible as Figure 9 and Table 4. A desorption tube from each set were re-run on the ATD/GC/MS before cleaning to verify all THMs were released from the tube. This is visible as Figure 8.

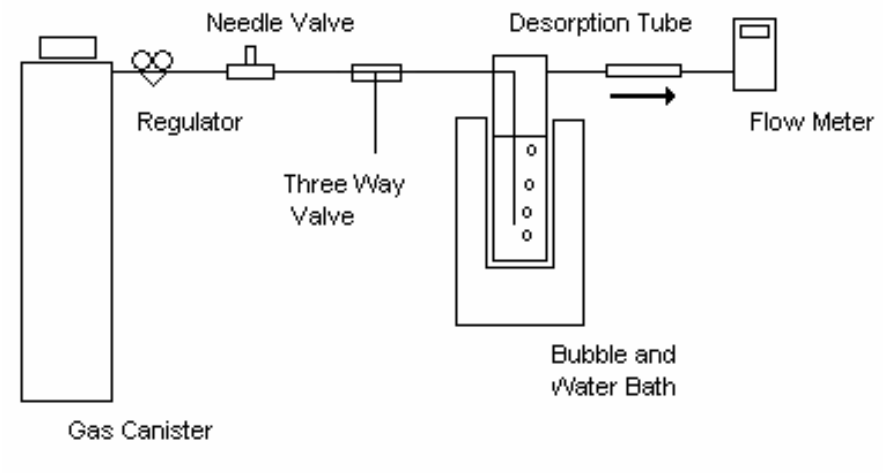

Figure 5: Schematic of First Purge and Trap Set-Up.

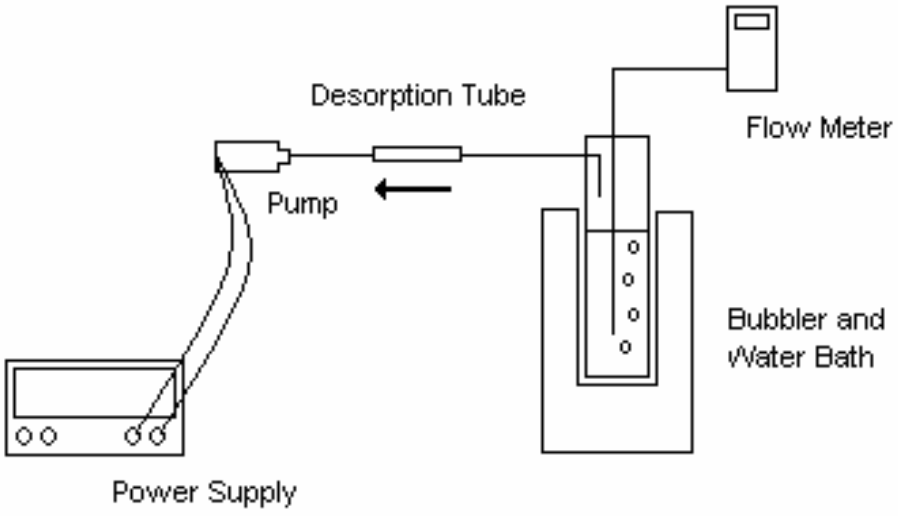

Figure 6: Schematic of Second Purge and Trap Set-Up.

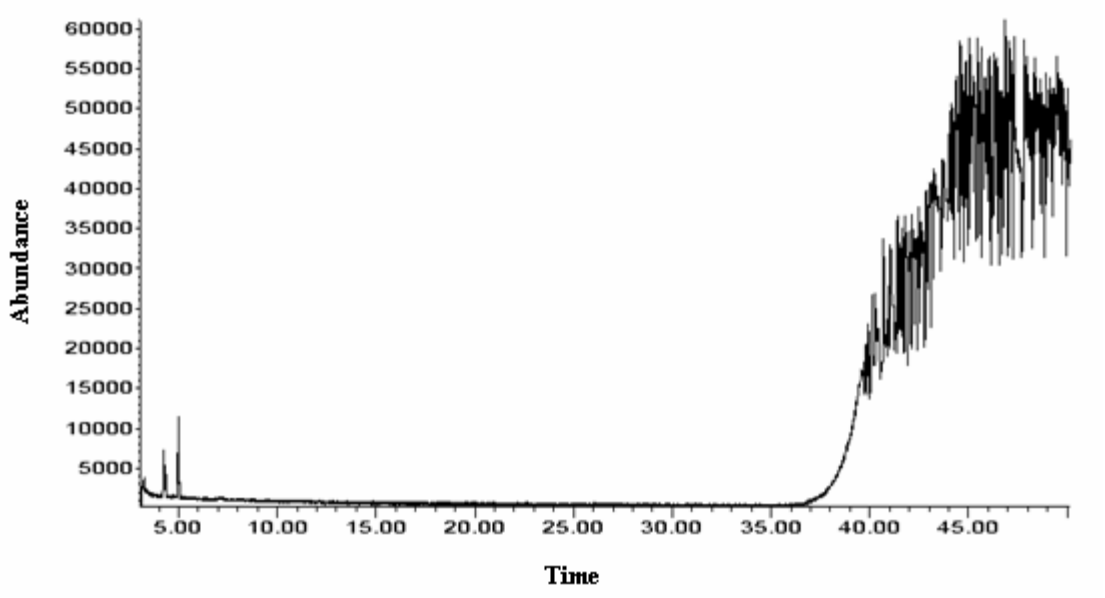

Figure 7: GC Chromatograph of a Cleaned Tenax TA Tube.

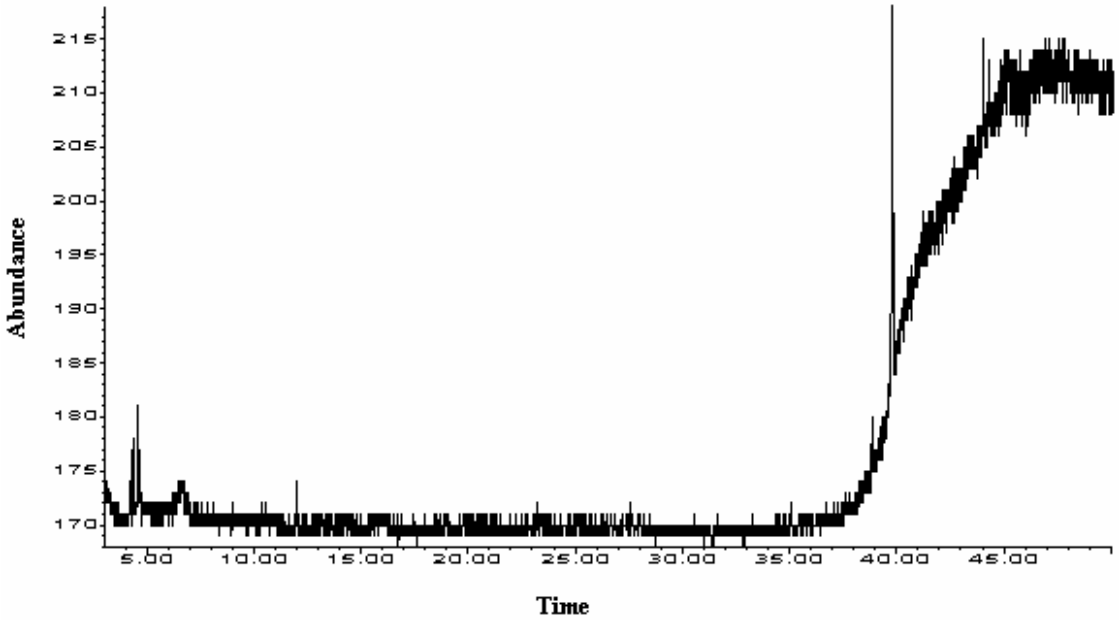

Figure 8: GC Chromatograph of a Tenax TA Tube Run After THM Desorption.

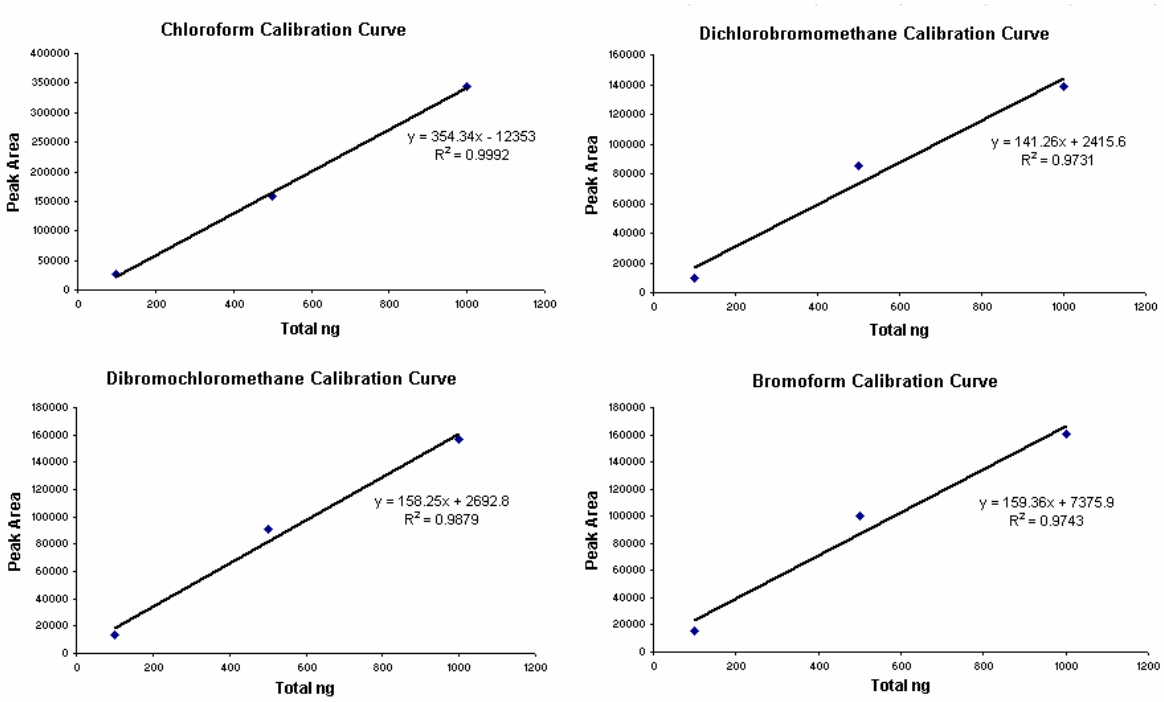

Figure 9: THM Calibration Curves.

Table 4: Data Used to Generate THM Calibration Curves.

	Chloroform	Dichlorobromomethane	Dibromochloromethane	Bromoform
100 ng	25,908 (5415)	9759 (165)	13,455 (536)	15,834 (566)
500 ng	159,725 (17,148)	85,254 (2275)	90,930 (4670)	100,517 (6773)
1000 ng	344,244 (45,240)	138,249 (285)	156,891 (3382)	160,753 (7291)

D. Results and Discussion

Aim 1: Compare the THM purging efficiency of compressed air and helium.

For this aim, the variable manipulated was the purging gas. A solution of 220 ppb was prepared in three steps. First, a solution of 110 ppm was made by mixing 1.5 ± 0.02 µL of chloroform into 20 mL of Milli-Q water. The amount of water was determined by weight using a Mettler AE 163 scale (Columbus, OH). Second, the 110 ppm solution was diluted 1:25 with water to produce a solution of 4400 ppb. Third, 1.25 mL of the 4400 ppb stock solution was mixed with 23.75 mL of water to generate a solution of 220 ppb (5500 ng). The 220 ppb solution was then purged with the first purge and trap system for 11 minutes at ambient temperature (20ºC). This process was repeated in triplicate using both helium and compressed air as the purging gas. The results are visible in Figure 10 and Table 5.

From the calibration curve above, it was determined that helium recovered 1355 ± 51 ng of chloroform while air recovered 1245 ± 103 ng. This resulted in a percent

recovery for helium and air of 29% and 27%, respectively. When compared directly, air purged 93% as effectively as helium. This result showed that environmental air is a suitable substitute for helium as a purging gas. It also disproved my hypothesis. Either the dipole moment of molecular oxygen and nitrogen does not interact with the THMs or THMs are so volatile the effect is negligible.

However, these results should be taken with modicum of skepticism. This is because the recoveries reported are substantially lower than those described in the literature. It has been reported that chloroform is the most volatile THM compound with a one hundred percent recovery after eleven minutes (a review of reported percent recoveries for all four THMs is found under Aim 2). Less than one-third of the expected recovery occurred. I suspect this discrepancy is primarily from flow inconsistencies in our system. This occurred in two ways. First, it was extremely difficult to maintain a constant flow using the needle valve. The needle valve was extremely sensitive with small bumps causing large flow changes. Second, although the Tenax TA® were commercially packed and purchased, flow restrictions between tubes changed. This meant different pressures were required to obtain a 40 cc flow. These two factors often resulted in it taking five or six minutes to get a 40 cc flow. This accounts for half of the purging time. During that time period, the flow through the desorption tube oscillated between too high and, more frequently, too low. Many samples were not purged with the full 440 cc of gas. Steps (eg, addition of the three-way valve) were taken to fix this issue, but it was never completely resolved. This problem was the primary reason a different system was used to test Aims 2 and 3. The power supply and miniature pump provided a better method for maintaining a constant flow. Unfortunately, it was not feasible at this time to use this system to test Aim 1 because the only available source of helium was a pressurized gas cylinder.

Aim 2: Evaluate how purge time affects the amount of THMs collected.

In this aim, the variable manipulated was the purging time. Ten milliliters of 100 µg/mL THM standard was mixed with 25 mL of Milli-Q water to generate a concentration of 40 µg/L or a solution containing 1000 ng of each THM. Water amount was determined by weight. The solution was then purged with air at 40 cc at ambient temperature (20ºC). Tubes were collected representing purge times of 1, 3, 5, 7, 9, 11, and 15 minutes. Each time was repeated in triplicate. The results are visible in Figure 11 and Table 6. It was determined that percent recovery was the greatest for dichlorobromomethane (144%) followed by dibromochloromethane (84%), chloroform (73%), and bromoform (54%).

These percent recoveries are interesting in two ways. First, the percent recovery for dichlorobromomethane was significantly greater than 100%. Second, our percent recoveries varied from those reported in the literature. A variety of recoveries have been reported using similar protocols[21, 23, 29, 31, 34] with the high and low recovery reported as follows: chloroform: 117 %[21], 86%[23]; dichlorobromomethane: 120%[21], 87%[23]; dibromochloromethane: 123%[21], 82%[31]; bromoform:124%[21], 63%[31]. Although some discrepancy exists, chloroform is the most volatile of the four THM. Dichloro-

bromomethane and dibromochloromethane are equal in volatility while bromoform is the least.

The differences between the literature and our results can be explained in the variations between our set-up and a commercial system. There are many. First, the flow variations discussed in Aim 1 still existed. Although a needle valve was no longer used and the pump/power supply provided quicker feedback, an iterative process was still needed to obtain a flow of 40 cc. All samples were not purged with full 440 cc of air. Second, unlike a commercial system where a single absorbent trap is used to collect all

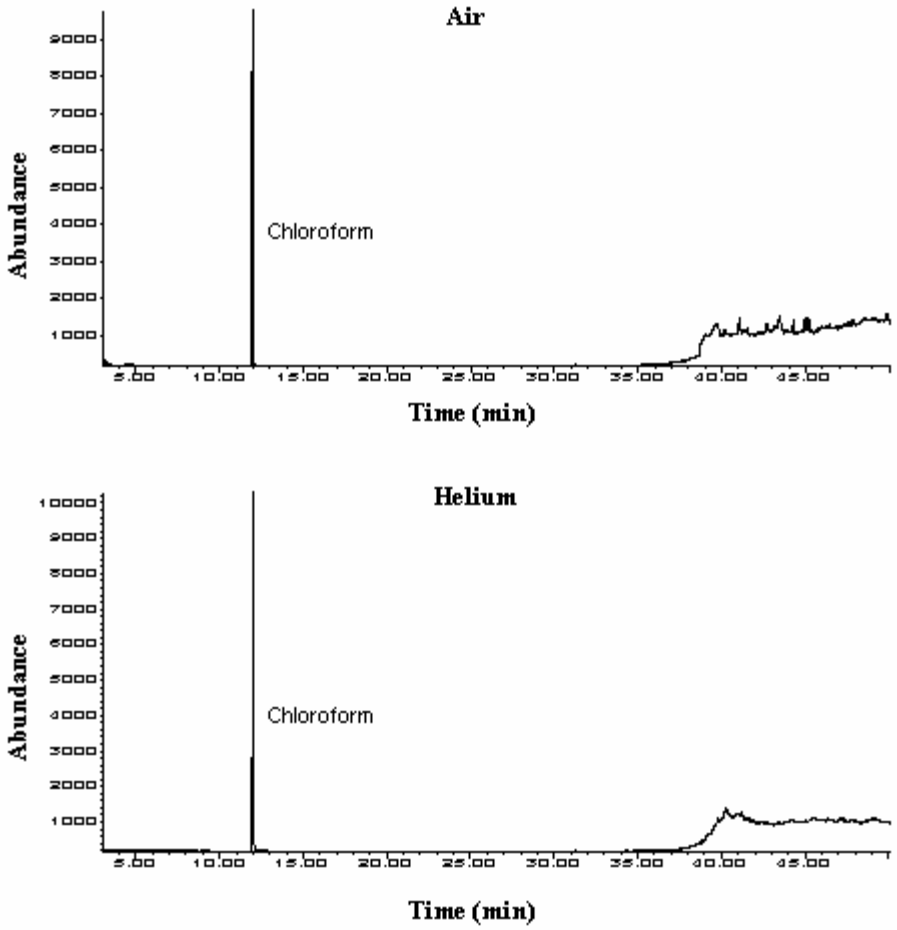

Figure 10: Chromatographs Comparing Peak Area Between Samples Purged with Helium (bottom) and Compressed Air (top) for 11 Minutes.

Table 5: Comparison of Helium and Air for Chloroform Recovery at 11 minutes.

	Peak Area	Chloroform Removed (ng)	Recovery (%)
Helium	492,677 (30,268)	1355 (51)	29 (1)
Air	453,490 (48,796)	1245 (103)	27 (2)

samples, our samples were collected on different tubes. This is because the purge and trap system was not integrated directly into GC/MS. The sample was collected, walked to the next room, and then run on the ATD/GC/MS. There provided opportunity for THMs to diffuse off the tube during this time period.

Although there is concern regarding the quantitative nature of these results, the qualitative nature is of importance. For this reason, a "comparative recovery" was calculated. It is visible in Table 5 and Figure 12. This recovery assumes that 100% of the THMs were removed at fifteen minutes and evaluates the percent of THM removed throughout each time period. .Power and time constraints make a shorter purge essential for success of the WASP system. With the exception of bromoform, more than fifty percent of the THMs were removed by fifteen minutes were removed at five minutes of purging. When evaluating at the preferred purge length of three minutes the "comparative recovery" values were as follows: chloroform (52%, 402 ng), dichlorobromomethane (43%, 612 ng), dibromochloromethane (37%, 305 ng), and bromoform (34%, 153ng). These results suggest my hypothesis is correct. They show that the majority of THM removal comes during the first five minutes. It is hopes that by purging for only three minutes enough THMs will be removed to be detected by the SAW.

Aim 3: Determine if the reservoir composition is important.

In this aim, the variable manipulated is the reservoir composition. EPA Method 524.2 specifies an all glass purging device to be used. The WASP system hopes to use a metal reservoir. Ten milliliters of 100 µg/mL THM standard was mixed with 25 mL of Milli-Q water to generate a concentration of 40 µg/L or a solution containing 1000 ng of each THM. Water amount was determined by weight. The solution was then purged with air at 40 cc at ambient temperature. Tubes were collected representing purge times of 1, 3, 5, 7, 9, 11, and 15 minutes. The experiment was not run in triplicate. The same data analysis was performed as for Aim 2.

The results are visible in Figure 13, Figure 14, and Table 7. It was determined that percent recovery was the greatest for dichlorobromomethane (163%) followed by dibromochloromethane (103%), chloroform (84%), and bromoform (68%). As compared to the glass reservoir, the overall percent recoveries were greater with the order remaining the same. These percent recoveries are also different from those reported in the literature. This is likely the result of the same problems described previously in Aim 2. A comparison in the actual recoveries is visible as Table 8.

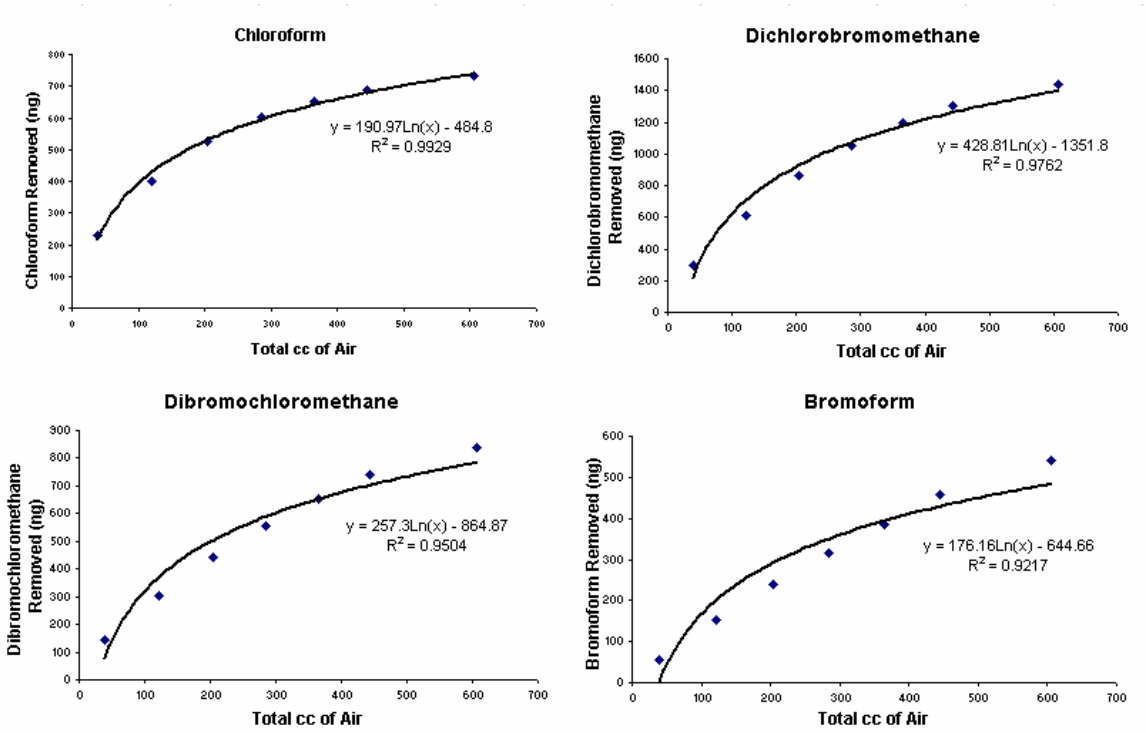

Figure 11: Removal of Each THM During a Fifteen-Minute Purge.
Initial spike level of 1000 ng, glass reservoir.

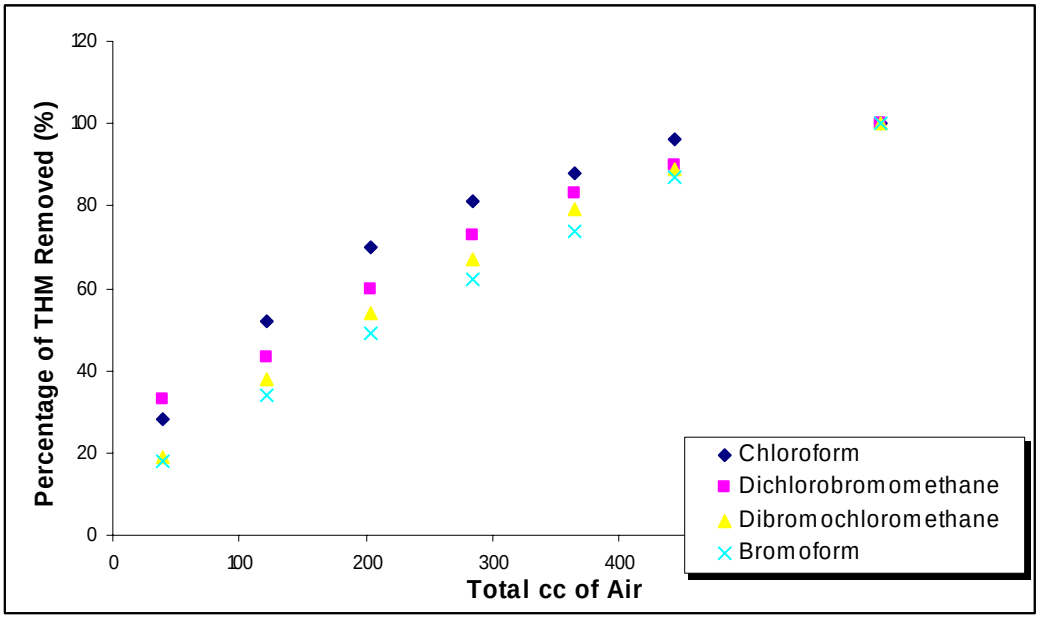

Figure 12: Comparative Recovery of Each THM.
Initial spike level of 1000 ng, glass reservoir.

Table 6: Comparison of THM Recoveries. Conditions: 1000 ng initial spike level, 15 minutes purge, purging with air, glass reservoir

	Chloroform			Dichlorobromomethane			Dibromochloromethane			Bromoform		
Time (min)	THM Removed (ng)	Actual Recovery[a] (%)	Comparative Recovery[b] (%)	THM Removed (ng)	Actual Recovery (%)	Comparative Recovery (%)	THM Removed (ng)	Actual Recovery (%)	Comparative Recovery (%)	THM Removed (ng)	Actual Recovery (%)	Comparative Recovery (%)
1	229 (68)	23 (7)	28 (2)	298 (34)	30 (3)	22 (0.5)	145 (3)	15 (0.3)	19 (2)	57 (30)	6 (3)	18 (0.5)
3	402 (102)	40 (10)	52 (3)	612 (107)	61 (11)	43 (2)	305 (43)	31 (4)	38 (1)	153 (9)	15 (0.9)	34 (2)
5	525 (118)	53 (12)	70 (3)	866 (137)	87 (14)	60 (3)	443 (60)	44 (6)	54 (3)	240 (2)	24 (0.2)	49 (4)
7	601 (124)	60 (12)	81 (3)	1047 (150)	105 (15)	73 (3)	554 (68)	55 (7)	67 (5)	315 (7)	32 (0.7)	62 (7)
9	654 (126)	65 (13)	88 (2)	1194 (162)	119 (16)	83 (3)	654 (79)	65 (8)	79 (5)	386 (17)	39 (2)	74 (7)
11	687 (126)	69 (13)	96 (2)	1301 (205)	130 (20)	90 (2)	740 (84)	74 (8)	89 (7)	458 (15)	46 (2)	87 (10)
15	734 (123)	73 (12)	100 (0)	1442 (195)	144 (20)	100 (0)	839 (139)	84 (14)	100 (0)	542 (62)	54 (6)	100 (0)

[a]Actual Recovery: Percent recovery compared to the initial spike level of 1000 ng.
[b]Comparative Recovery: Percent recovery assuming that 100% of the material was extracted at 15 minutes.

The major difference between the glass and metal reservoir is seen in the comparative recoveries. Although more THMs were removed overall, fewer THMs were removed in the first three minutes. The results were as follows: chloroform (46%, 405 ng), dichlorobromomethane (35%, 567 ng), dibromochloromethane (32%, 321), and bromoform (28%, 160 ng). None of the THMs had a "comparative recovery" greater than fifty percent for the first three minutes. These percentages are deceiving because the actual amount of THM collected at three minutes is greater than with a glass reservoir. SAW detection limits should then also be met with a metal reservoir. This suggests our hypothesis was correct. A metal reservoir composed of stainless steel can be used without impacting the percent recoveries.

E. Conclusion

Several conclusions were made by this project.

- Environmental air can be used as a substitute for helium as a purging gas. Compressed air purged 93% as effectively as helium.

- The majority of THM removal occurring during the first five minutes of purging. By purging for only three minutes it is likely a sufficient amount THMs will be removed for detection by the SAW.

- A metal reservoir can be used as a substitute for glass.

THM formation is a problem gaining international attention. Other countries have followed the United States and placed their own regulations on THM exposure. These standards include 350 ppb in Canada, 100 ppb in the United Kingdom, 10 ppb in Germany, and 1 ppb in Holland.[8] If these regulations are to be followed, then a better understanding THM formation and more cost-effective method for THM detection needs to be developed. Both EPA 524.2 and AWWA 6200 methods depend on purge and trap for THM extraction to the gas phase. However, purge and trap has two main drawbacks: the slowness of the purging step and the high detection limits. These drawbacks are partially solved by WASP through use of SAW detectors. SAW detectors are smaller and have greater sensitivity then many conventional methods. Their size makes the amiable to a field system and their increased sensitivity means a shorter purging step can be utilized. This is allows the WASP to weigh less than 32 pounds, occupy a carry-on luggage sized case, and perform analysis is less than four minutes[22].

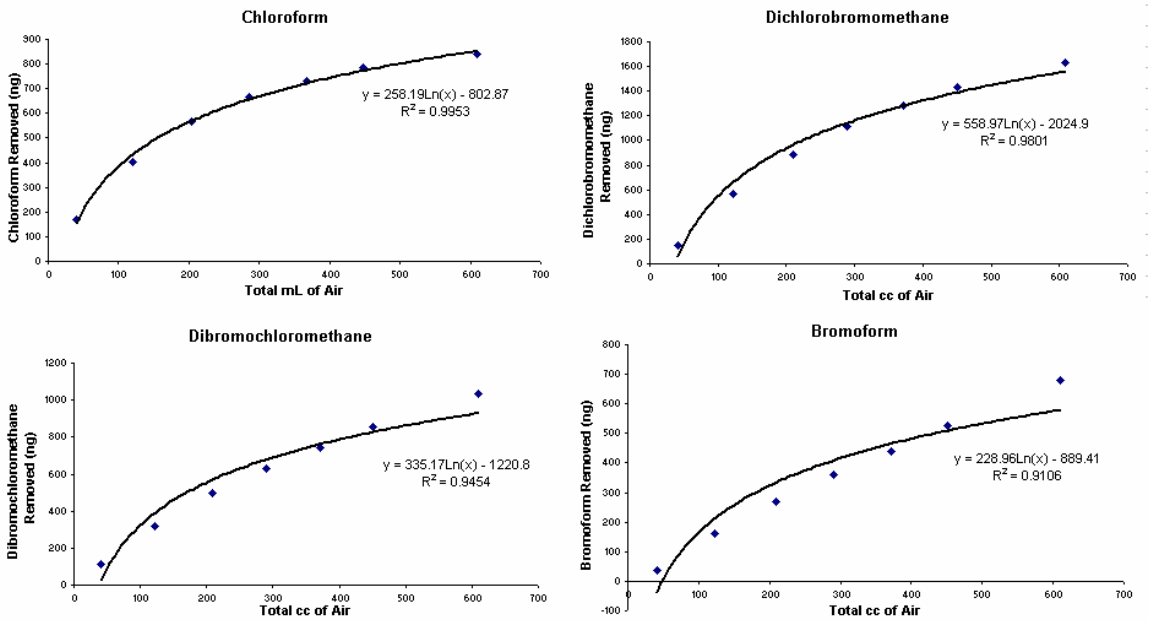

Figure 13: Removal of Each THM During a Fifteen-Minute Purge.
Initial spike level of 1000 ng, metal reservoir.

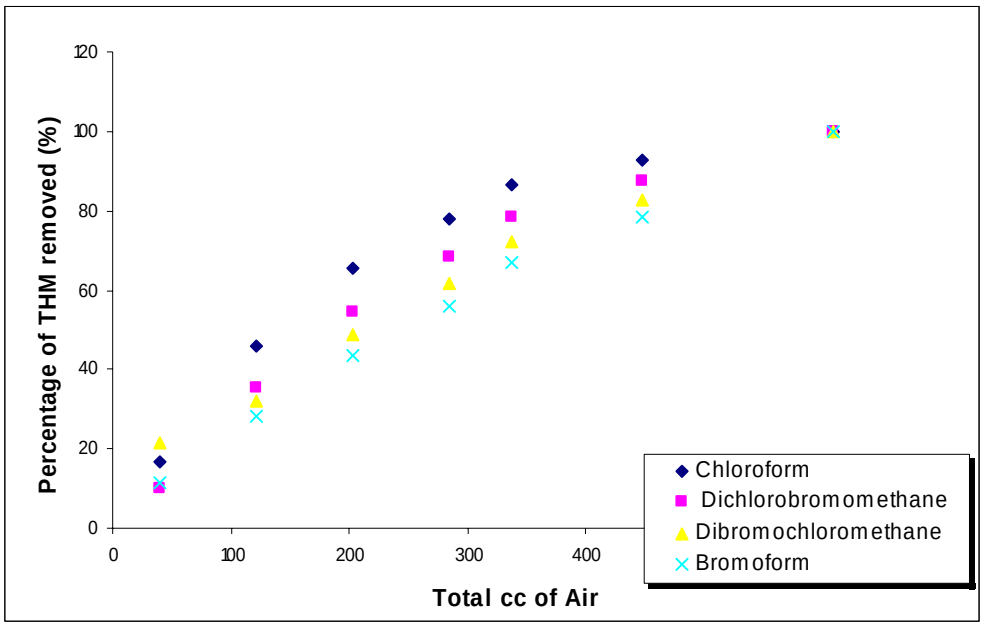

Figure 14: Comparative Recovery for Each THM.
Initial spike level of 1000 ng, metal reservoir.

Table 7: Comparison of THM Recoveries.

Conditions: 1000 ng initial spike level, 15 minutes purge, purging with air, metal reservoir

	Chloroform			Dichlorobromomethane			Dibromochloromethane			Bromoform		
Time (min)	THM Removed (ng)	Actual Recovery (%)	Comparative Recovery (%)	THM Removed (ng)	Actual Recovery (%)	Comparative Recovery (%)	THM Removed (ng)	Actual Recovery (%)	Comparative Recovery (%)	THM Removed (ng)	Actual Recovery (%)	Comparative Recovery (%)
1	167	17	17	148	15	10	113	11	21	36	4	11
3	405	40	46	567	57	35	321	32	32	160	16	28
5	565	56	66	886	89	55	495	50	49	270	27	43
7	666	66	78	1112	111	68	629	63	62	360	36	56
9	733	73	87	1282	128	79	741	74	72	440	44	67
11	784	78	93	1429	143	88	852	85	83	525	52	79
15	842	84	100	1634	163	100	1033	103	100	681	68	100

Table 8: Comparison of Actual Recoveries Using Glass and Metal Reservoirs.

	Chloroform			Dichlorobromomethane			Dibromochloromethane			Bromoform		
Time (min)	Recovery: Glass (%)	Recovery: Metal (%)	Difference (%)	Recovery: Glass (%)	Recovery: Metal (%)	Difference (%)	Recovery: Glass (%)	Recovery: Metal (%)	Difference (%)	Recovery: Glass (%)	Recovery: Metal (%)	Difference (%)
1	23 (7)	17	6	30 (3)	15	15	15 (0.3)	11	4	6 (3)	4	2
3	40 (10)	40	0	61 (11)	57	4	31 (4)	32	1	15 (0.9)	16	1
5	53 (12)	56	3	87 (14)	89	2	44 (6)	50	6	24 (0.2)	27	3
7	60 (12)	66	6	105 (15)	111	6	55 (7)	63	8	32 (0.7)	36	4
9	65 (13)	73	8	119 (16)	128	8	65 (8)	74	9	39 (2)	44	5
11	69 (13)	78	9	130 (20)	143	13	74 (8)	85	11	46 (2)	52	6
15	73 (12)	84	11	144 (20)	163	19	84 (14)	103	19	54 (6)	68	14

It is known that multiple factors affect THM formation: total concentration of organic carbon, pH, temperature, and chlorine type/dosage.[8] It is also know that THM formation follows seasonal patterns. The mechanism by how these factors interact still remains a mystery. Monitoring more surface water sources more frequently provides numerous opportunities to better understand THM development. This knowledge is essential for controlling THM formation in the future and minimizing the affect on human heath.

It is further hoped that WASP has uses beyond THM detection. EPA Method 524.2 lists over seventy compounds for which purge and trap is the preferred method for removal. Research should be continued using WASP in the monitoring of other environmental contaminants or biological/chemical warfare agents (ex. methyl salicylate, dimethyl methylphosphonate, and diethyl methylphosphonate). As expressed in the specific aims, this project planned to evaluate the effectiveness of purge and trap removal for some of these compounds. Unfortunately, this did not occur due to financial and time constraints. The compound of greatest interest was methyl tert-butyl ether (MTBE). MTBE is an oxygenate added to gasoline to improve combustion.[35] Oxygenates have high water solubility and MTBE has been found contaminating multiple water supplies. The effect of MTBE consumption has not been well established causing the US EPA and counterpart agencies in Japan to develop guidelines to limit or eliminate its use.[36] Since a cost-effective and efficient method for MTBE detection is lacking, EPA has argued that a complete ban is justified. SNL's WASP system has the potential to fill this gap in technology.

The development of WASP occurred through the collaboration of many talented individuals. Although the full system is discussed in this paper, I was not involved in many aspects of the WASP project. My contribution was strictly in characterizing differences in purge and trap in a laboratory set-up compared to WASP. This research focused on the purging gas, time, and reservoir composition.

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